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(54) **Low fluid loss heavy brines containing hydroxyethyl cellulose**

(57) Hydroxyethyl cellulose can function as a fluid loss additive containing 16 to 20% by weight of zinc bromide and either or both of calcium chloride and calcium bromide. When the concentration (X) of zinc bromide exceeds 20% by weight, both calcium chloride and calcium bromide must be present, the concentration of calcium chloride being at least (2X—33)% by weight.

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SPECIFICATION

Low fluid loss heavy brines containing hydroxyethyl cellulose

The present invention relates to heavy brine solutions containing zinc bromide and at least one soluble salt selected from the group consisting of calcium chloride and calcium bromide, and, in particular, to such brines having a low fluid loss containing hydroxyethyl cellulose.

In recent years, the practical operating range of clear brines for use in the oil and gas industry has been significantly extended by utilizing soluble zinc salts, particularly zinc bromide, so that the advantages of clear brines can now be obtained with fluids having densities as high as 2.3 g/cm^3 at ambient temperatures and pressures.

The high density clear brines are used extensively: e.g. as completion fluids to minimize plugging of perforation tunnels, to protect formation permeability and to minimize mechanical problems; as workover fluids, for the same reasons; as packer fluids, to allow easy movement and retrieval of the packer; for underreaming, gravel-pack and sand consolidation applications; as kill fluid or ballast fluid; for wire-line work; and as drilling fluids.

Clear brines having a density of up to 1.7 g/cm^3 are generally formulated to contain sodium chloride, sodium bromide, potassium chloride, calcium chloride, calcium bromide, or mixtures of these salts. Clear brines having a density up to 1.81 g/cm^3 can be formulated with calcium chloride and calcium bromide. If the brine must have a low crystallization temperature, however, then clear brines in this density range are generally formulated to contain a soluble zinc salt. Zinc bromide is preferred because brines containing it are less corrosive than brines containing zinc chloride. Clear brines having a density greater than 1.81 g/cm^3 are formulated to contain zinc bromide.

Generally, hydroxyethyl cellulose (HEC) and xanthan gum polymers are compatible with those fluids which do not contain zinc salts. At higher densities, however, the rate of hydration of these viscosifiers is significantly slower. HEC is generally considered as unsatisfactory for use in fluids containing zinc salts.

The present invention provides a heavy brine solution containing (a) at least 16% by weight of zinc bromide, (c) calcium chloride and/or calcium bromide, and (c) sufficient hydroxyethyl cellulose to reduce the fluid loss of said brine, with the proviso that when the brine contains more than 20% by weight of zinc bromide, it also contains both calcium chloride and calcium bromide, calcium chloride being present in an amount of at least (2X − 33)% by weight, where X is the weight percentage of zinc bromide in the brine.

The present invention also provides a method of reducing the fluid loss of a heavy brine solution containing (a) at least 16% by weight of zinc bromide, and (b) calcium chloride and/or calcium bromide with the proviso that when the brine contains more than 20% by weight of zinc bromide, it also contains both calcium chloride and calcium bromide, calcium chloride being present in an amount of at least (2X − 33)% by weight, where X is the weight percentage of zinc bromide in the brine, which method comprises mixing the brine with sufficient hydroxyethyl cellulose to reduce its fluid loss.

We have now found that HEC will function as a fluid loss additive in certain heavy brines in which it does not function efficiently as a viscosifier. These heavy brines contain either:

1) from 16 to 20% by weight of zinc bromide and either or both of calcium chloride and calcium bromide; or

2) more than 20% by weight of zinc bromide and both calcium chloride and calcium bromide, the concentration of calcium chloride being at least (2X − 33)% by weight.

The heavy brines for use in the present invention contain zinc bromide and at least one soluble salt selected from calcium chloride and calcium bromide.

In one embodiment of the invention, the concentration of zinc bromide is from 16 to 20% by weight. Preferably the concentration of zinc bromide is ≤18% by weight and the concentration of calcium chloride is ≤5(X − 17)% where X is the weight percentage of zinc bromide.

In another embodiment of the invention, the brine contains more than 20% by weight of zinc bromide and a concentration of calcium chloride of at least (2X − 33)% by weight.

The preferred brines have a density in the range from about 1.70 to 1.92 g/cm^3.

Generally, heavy brines are prepared by mixing together various standard commercially-available brines, as follows: calcium chloride brines having a density in the range from 1.318 to 1.30 g/cm^3; calcium bromide brine having a density of 1.702 g/cm^3; and a calcium bromide/zinc bromide solution having a density of 2.300 g/cm^3 containing about 20% by weight of calcium bromide and about 57% by weight of zinc bromide. Solid calcium chloride and solid calcium bromide are also used in conjunction with these brines to prepare the heavy brines for use in this invention. It is, however, preferred to use only liquid solutions to formulate the brines in the practice of this invention. Standard brine mixing/preparation tables are available from the various manufacturers and suppliers of these commercially available brines.

The HEC polymers which are useful as fluid loss control agents in accordance with the present invention are solid, particulate materials which are water soluble or water dispersible gums and which upon solution or dispersion in an aqueous medium increase the viscosity of the system. HEC polymers are generally high yield, water soluble, non-ionic materials produced by treating cellulose with sodium

hydroxide followed by reaction with ethylene oxide. Each anhydroglucose unit in the cellulose molecule has three reactive hydroxy groups. The average number of moles of the ethylene oxide that becomes attached to each anhydroglucose unit in cellulose is called "moles of substituent combined". The average number of hydroxyl groups of each anhydroglucose unit which is reacted with ethylene oxide is called the degree of substitution. In general, it is preferable to use HEC polymers having a mole substitution greater than 1.

Usually, upon the addition of dry, powdered hydrophilic polymers, such as HEC, to water, the polymer particles undergo hydration preventing the interior of the particle from readily hydrating, solvating or otherwise dispersing in the aqueous medium. Accordingly, high shear, long mixing times and/or elevated temperatures must be applied in order to obtain a homogeneous system.

We have described methods by which HEC and other hydrophilic polymers can be activated such that the polymers will viscosify heavy brines at ambient temperatures. Activated HEC compositions, and methods for activating HEC, are disclosed in our published British Patent Applications No. 2070611A and 2075041A. Methods of activating other hydrophilic polymers are disclosed in our published British Patent Application No. 2086923A.

Typical activated HEC compositions comprise:

1) HEC, a solvating agent comprising a water miscible, polar organic liquid which when uniformly mixed with HEC in a weight ratio of HEC to solvating agent of 1:2 produces a mixture with substantially no free liquid solvating agent present after remaining quiescent for one week at ambient temperature in a sealed container, and a diluting agent comprising an organic liquid which is not a solvating agent; and

2) HEC, an aqueous liquid, and a water soluble polar organic liquid which when uniformly mixed with HEC in a weight ratio of HEC to polar organic liquid of 1:2 produces a mixture with free liquid present after remaining quiescent for one week at ambient temperature in a sealed container. Preferably the aqueous liquid has a pH greater than 7.0.

Generally speaking, it has been found that virtually any organic compound which passes the solvation test described above, will function, to a usable degree, as a solvation agent. Non-limiting but preferred solvating agents include: aliphatic glycols containing from 2 to 5 carbon atoms such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, and 1,3-pentanediol; alkylene triols containing from 2 to 6 carbon atoms such as glycerol, 1,2,3-butane-triol, and 1,2,3-pentanetriol; amides containing from 1 to 4 carbon atoms such as formamide, acetamide, and dimethyl formamide; and mixtures of the various above compounds.

The diluting agent, in general, will be any liquid organic compound or material which is not a solvating agent. In general, the diluting agents are liquids which do not appreciably swell the HEC polymers, i.e. they do not produce semi-solid or viscous mixtures which have no free liquid present after the one week solvation period described in the above test for determining solvating agents. Non-limiting examples of diluting agents include liquid aliphatic and aromatic hydrocarbons containing from 5 to 10 carbon atoms, kerosene, diesel oil, isopropanol, alkylene glycol ethers, and vegetable oils. Particularly preferred are organic liquids which are water soluble or miscible, most preferably alkanols having at least 3 carbon atoms, ethylene glycol monoalkyl ethers, and dialkylene glycol monoalkyl ethers. The diluting agent will maintain the polymeric composition in a liquid, pourable state at a temperature of about 20°C. It will be understood, however, that lesser amounts of diluting agent can be used if desired, and that the ultimate amount of diluting agent employed will depend upon the type of shear which is available to disperse the thickener. In general it has been found that desirable thickeners, which are pourable liquids, can be produced from compositions containing from 10 to 25% by weight of HEC polymer, from 2 to 70% by weight of diluting agent, and from 5 to 88% by weight of solvating agent.

HEC has been added to heavy brines to increase the viscosity of the brine such that the rate of loss of the brine to the formation contacted by the brine is reduced. Normally, in the absence of bridging particles, hydroxyethyl cellulose provides poor fluid loss control in those brines in which the HEC is fully hydrated. See for example, our prior British Patent Application No. 8131312, which indicates that if the concentration of zinc bromide is less than 20% by weight, the HEC will not efficiently gel or viscosify the brine. Indeed, we have found that while it is possible to viscosify with HEC a brine containing no zinc bromide, or a brine solution containing a high concentration of zinc bromide, if two such thickened solutions are mixed to produce a solution containing zinc bromide in a concentration of less than 20% by weight, the viscosity of the mixed brine will be substantially the same as if no HEC is present.

It is a feature of the present invention that HEC functions as an excellent fluid loss control additive in certain heavy brines in which the HEC is a very inefficient viscofier. The HEC-containing brines of this invention are cloudy or opaque as compared to the clear brines obtained when the HEC is completely, or nearly completely, hydrated. Apparently the HEC is not completely solubilized in these brines and thus at least a portion of the HEC is available to act as a bridging agent to decrease the fluid loss of these brines.

It is preferred in the practice of this invention that the HEC be activated such that the HEC will hydrate in these heavy brines at ambient temperature.

The concentration of HEC need only be sufficient to reduce the fluid loss of the brine. Preferably, the concentration of HEC will be from 0.7 to 14.3 g/l, more preferably, 0.7 to 8.6 g/l.

The following non-limiting Examples are presented to illustrate the invention more fully.

All percentages are by weight unless otherwise indicated.

EXAMPLES

Heavy brines having the compositions listed in Table 1 were prepared by mixing together the indicated amounts of the following materials: (A) a 2.301 g/cm³ calcium bromide/zinc bromide solution containing 20% of calcium bromide and 57% of zinc bromide; (B) a 1.702 g/cm³ calcium bromide solution containing 53% of calcium bromide; (C) a 1.390 g/cm³ calcium chloride solution containing 37.6% of calcium chloride; and calcium chloride pellets containing 95% of calcium chloride. After cooling to room temperature, there were added either: 8.559 g/l of NATROSOL 250 HHR hydroxyethyl cellulose; or 8.559 g/l of activated NATROSOL 250 HHR (i.e., 42.795 g/l of a composition containing 20% of HEC, 25% of glycerin, 54.6% of isopropanol, and 0.4% of CAB-O-SIL M5). Thereafter, the heavy brines were rolled 16 hours at room temperature and the API RP 13B rheology and fluid loss obtained. The heavy brines were then rolled 16 hours at 65.5°C, cooled at room temperature, and the API RP 13B data again obtained. The data obtained are given in Table 2.

The data indicate that heavy brines containing HEC can be formulated to exhibit a very low API fluid loss provided the zinc bromide concentration in the brine is in the range from 16% to 20% by weight, or the zinc bromide concentration is greater than 20% and the calcium chloride concentration is greater than $(2X - 33)\%$ where X is the percentage of zinc bromide in the brine. Preferably, the zinc bromide concentration is in the range from 18 to 20% and the calcium chloride concentration is less than about $5(X - 17)\%$. In this preferred range the HEC solubilizes to such an extent that appreciable viscosity is imparted to the heavy brine. The data also indicate that it is preferable to omit any solid calcium chloride from the heavy brine.

TABLE 1
Brine Compositions

Example	Density (g/cm³)	% $ZnBr_2$	% $CaCl_2$	% $CaBr_2$	A (l)	C (l)	B (l)	95% $CaCl_2$ (Kg)
1	1.797	0	16.3	43.3	0	4.53	137.30	46.66
2	1.797	0	16.3	43.3	0	4.53	137.30	46.66
3	1.833	5.1	14.9	41.2	11.35	4.31	127.40	43.35
4	1.833	5.1	14.9	41.2	11.35	4.31	127.40	43.35
5	1.797	11.7	0	46.2	25.44	0	133.53	0
6	1.797	11.7	0	46.2	25.44	0	133.53	0
7	1.893	13.2	12.5	38.0	30.20	3.64	111.28	37.78
8	1.893	13.2	12.5	38.0	30.20	3.64	111.28	37.78
9	1.833	15.7	0	43.9	34.97	0	124.00	0
10	1.833	15.7	0	43.9	34.97	0	124.00	0
11	1.833	16.0	0	43.7	35.61	0	123.36	0
12	1.773	16.0	5.0	36.8	34.50	27.02	97.45	0
13	1.726	16.0	10.0	29.6	33.46	52.46	73.05	0
14	1.917	16.3	11.6	36.7	37.83	3.40	104.60	35.56
15	1.917	16.3	11.6	36.7	37.83	3.40	104.60	35.56
16	1.845	17.0	0	43.1	37.99	0	120.98	0
17	1.785	17.0	5.0	36.1	36.83	27.18	94.95	0
18	1.857	18.0	0	42.5	40.54	0	118.43	0

TABLE 1—*Continued*

Example	Density (g/cm^3)	% $ZnBr_2$	% $CaCl_2$	% $CaBr_2$	A (l)	C (l)	B (l)	95% $CaCl_2$ (Kg)
19	1.797	18.0	5.0	35.5	39.19	27.34	92.44	0
20	1.767	18.0	7.5	32.0	38.58	40.33	80.06	0
21	1.738	18.0	10.0	28.5	37.99	53.10	67.88	0
22	1.857	18.4	0	42.4	41.33	0	117.64	0
23	1.857	18.4	0	42.4	41.33	0	117.64	0
24	1.857	19.0	0	42.1	42.92	0	116.05	0
25	1.809	19.0	5.0	34.8	41.57	27.58	89.82	0
26	1.750	19.0	10.0	28.0	40.30	53.02	65.65	0
27	1.708	19.0	14.0	22.3	39.33	72.70	46.94	0
28	1.869	20.0	0	41.5	45.37	0	113.58	0
29	1.773	20.0	8.0	30.2	43.14	43.38	72.44	0
30	1.773	20.0	8.0	30.2	43.14	43.38	72.44	0
31	1.714	20.0	14.0	21.7	41.55	73.13	44.29	0
32	1.714	20.0	14.0	21.7	41.55	73.13	44.29	0
33	1.917	22.0	11.7	31.0	51.09	19.08	78.80	26.86
34	1.917	22.0	11.7	31.0	51.09	19.08	78.80	26.86
35	1.750	22.0	12.0	23.4	46.78	64.03	48.15	0
36	1.750	22.0	12.0	23.4	46.78	64.03	48.15	0
37	1.726	22.0	14.0	20.7	46.10	73.57	39.30	0
38	1.726	22.0	14.0	20.7	46.10	73.57	39.30	0

Examples 1 to 10 are Comparison Examples.

TABLE 2
Brine Evaluations

8.559 g/l NATROSOL 250 HHR(1)

	16 Hours @ 23°C				16 Hours @ 65.5°C			
	API Rheology			API Fluid Loss(2)	API Rheology			API Fluid Loss
Example	600	300	3		600	300	3	
1	>300	>300	130	23	>300	>300	149	60
2	(68)	(35)	(0)	(20)	(>300)	(>300)	(69)	(80)
3	56	29	2	125	67	34	1	NC
4	(62)	(31)	(0)	(NC)	(60)	(30)	(1)	(187)
5	15	8	0	NC	32	16	0	3
6	(14)	(7)	(0)	(NC)	(16)	(8)	(0)	(18)
7	51	26	0	131	63	32	2	NC
8	(49)	(25)	(0)	(NC)	(51)	(26)	(0)	(150)
9	24	12	0	NC	98	36	1	1
10	(15)	(7)	(0)	(NC)	(40)	(24)	(2)	(4)
11	44	23	1	22	58	30	1	1
12	24	11	0	NC	33	15	0	4
13	21	11	0	NC	44	17	0	9.5
14	50	25	0	103	63	31	0	NC
15	(52)	(26)	(0)	(NC)	(49)	(25)	(0)	(120)
16	42	22	0	5	61	34	3	1
17	32	16	1	25	55	30	2	1
18	222	153	35	1	283	198	37	1
19	162	106	15	1	192	127	11	1
20	31	115	0	50	47	25	3	1
21	57	31	1	16	62	32	1	2
22	205	158	33	1	>300	184	44	1
23	(15)	(8)	(1)	(NC)	(50)	(25)	(1)	(2)
24	222	196	52	1	>300	227	59	1
25	193	161	39	1	274	198	46	1
26	158	104	12	1	187	120	10	1
27	41	21	0	4	52	28	1	1

TABLE 2—*Continued*

8.559 g/l NATROSOL 250 HHR[1]

	16 Hours @ 23°C				16 Hours @ 65.5°C			
	API Rheology			API Fluid Loss[2]	API Rheology			API Fluid Loss
Example	600	300	3		600	300	3	
28	202	218	57	1	>300	249	76	1
29	230	161	34	0	264	205	41	3
30	(14)	(8)	(0)	(NC)	(63)	(33)	(1)	(1)
31	152	101	9	1	>300	233	57	5
32	(14)	(7)	(0)	(NC)	(48)	(24)	(1)	(2)
33	46	23	1	29	172	101	5	1
34	(37)	(19)	(0)	(NC)	(47)	(24)	(0)	(2)
35	234	191	42	4	212	197	44	4
36	(16)	(8)	(0)	(NC)	(103)	(59)	(1)	(0.5)
37	229	170	39	2	213	140	11	5
38	(16)	(8)	(0)	(NC)	(77)	(41)	(1)	(0.2)

[1] Data in parentheses obtained using dry, powdered NATROSOL 250 HHR.
[2] NC = No Control.

CLAIMS

1. A heavy brine solution containing (a) at least 16% by weight of zinc bromide, (b) calcium chloride and/or calcium bromide, and (c) sufficient hydroxyethyl cellulose to reduce the fluid loss of said brine, with the proviso that when the brine contains more than 20% by weight of zinc bromide, it also contains both calcium chloride and calcium bromide, calcium chloride being present in an amount of at least (2X − 33)% by weight, where X is the weight percentage of zinc bromide in the brine.

2. A brine as claimed in Claim 1 which comprises from 16 to 20% by weight of zinc bromide.

3. A brine as claimed in Claim 1 which comprises (a) zinc bromide, and (b) both calcium chloride, and calcium bromide, the amount of zinc bromide being greater than 20% by weight and the concentration of calcium chloride being at least (2X − 33)% by weight, where X is the weight percentage of zinc bromide in the brine.

4. A brine as claimed in any preceding Claim, which has a density from 1.70 to 1.92 g/cm^3.

5. A brine as claimed in any preceding Claim which contains from 0.70 to 14.3 g/l of hydroxyethyl cellulose.

6. A brine as claimed in Claim 5 which contains from 0.7 to 8.6 g/l of hydroxyethyl cellulose.

7. A brine as claimed in any preceding Claim wherein the hydroxyethyl cellulose has been activated such that it will hydrate in said brine at ambient temperatures.

8. A method of reducing the fluid loss of a heavy brine solution containing (a) at least 16% by weight of zinc bromide, and (b) calcium chloride and/or calcium bromide with the proviso that when the brine contains more than 20% by weight of zinc bromide, it also contains both calcium chloride and calcium bromide, calcium chloride being present in an amount of at least (2X − 33)% by weight, where X is the weight percentage of zinc bromide in the brine, which method comprises mixing the brine with sufficient hydroxyethyl cellulose to reduce its fluid loss,

9. A method as claimed in Claim 8 wherein the brine contains from 16 to 20% by weight of zinc bromide.

10. A method as claimed in Claim 8 wherein the brine contains at least 20% by weight of zinc bromide as well as both calcium chloride and calcium bromide, the concentration of calcium chloride being at least (2X − 33)% by weight, where X is the weight percentage of zinc bromide, in the brine.

11. A method as claimed in any of Claims 8 to 10 wherein said brine has a density from 1.70 to

1.92 g/cm^3.

12. A method as claimed in any of Claims 8 to 11 wherein the brine contains from 0.7 to 14.3 g/l of hydroxyethyl cellulose.

13. A method as claimed in Claim 12 wherein the brine contains from 0.7 to 8.6 g/l of hydroxyethyl cellulose.

14. A method as claimed in any of Claims 8 to 13, wherein the hydroxyethyl cellulose has been activated such that it will hydrate in said brine at ambient temperatures.

15. A brine as claimed in Claim 1 and substantially as hereinbefore described with reference to

16. A method as claimed in Claim 8 and substantially as hereinbefore described with reference to

17. Brine whose fluid loss as reduced by a method as claimed in any of Claims 8 to 14 and 16.

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